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MEMORANDUM FOR PRS (In-House/Contractor Publication)

FROM: PROI (STINFO) 28 Feb 2003

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2003-049**
Joseph M. Mabry (ERC); Rusty L. Blanski; Patrick N. Ruth; Capt. Rene I. Gonzalez, "Fluorinated POSS"

American Chemical Society Conference **(Statement A)**
(New Orleans, LA, 23-27 Mar 2003) (Deadline: 21 Mar 2003)

Fluorinated POSS

Joseph M. Mabry,[1*] Rusty L. Blanski,[2]
Patrick N. Ruth,[1] and Rene I. Gonzalez[2]

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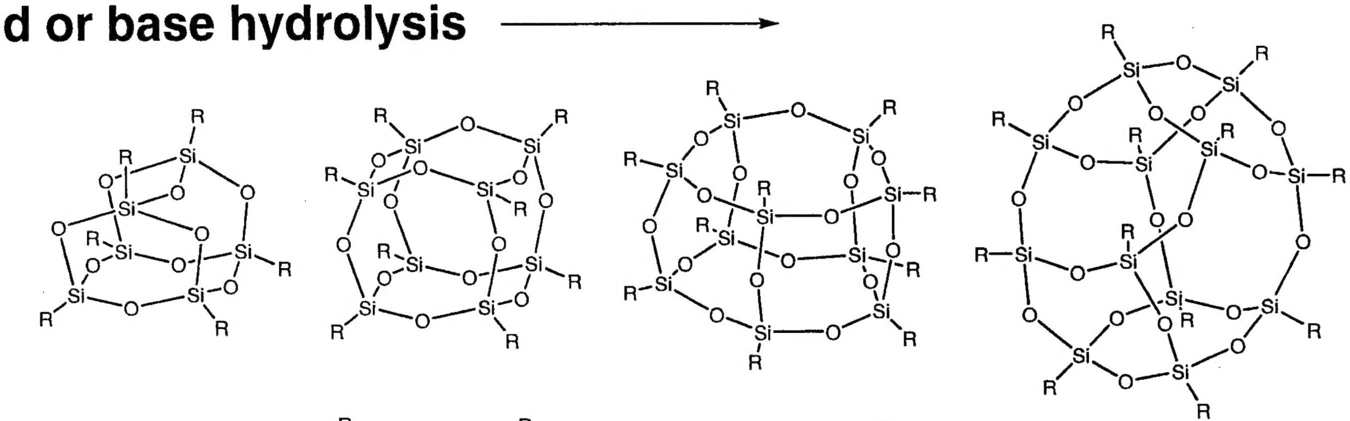
Edwards Air Force Base, CA 93524

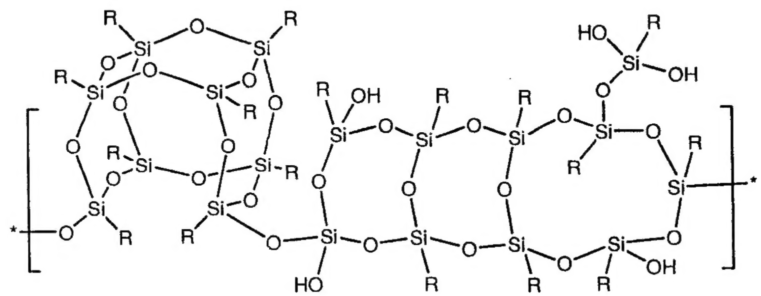
POSS Synthesis

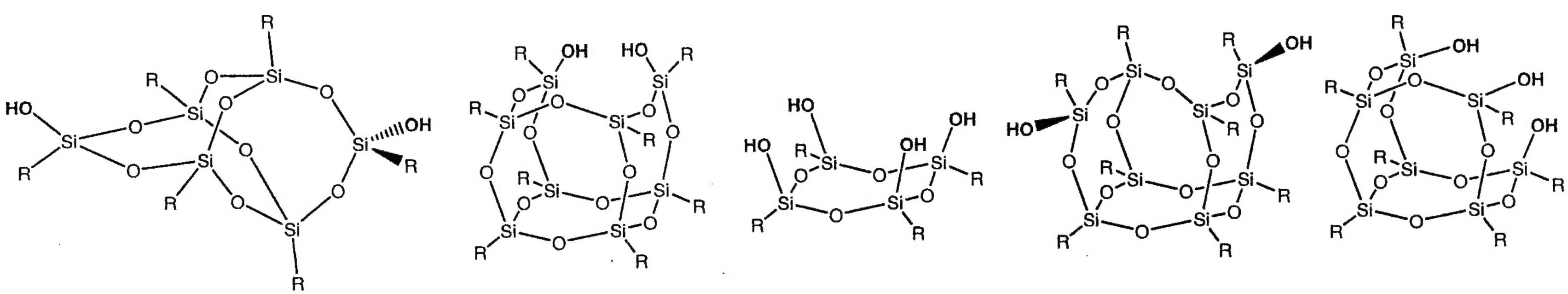
$RSiX_3$ acid or base hydrolysis →

Completely condensed



Resin

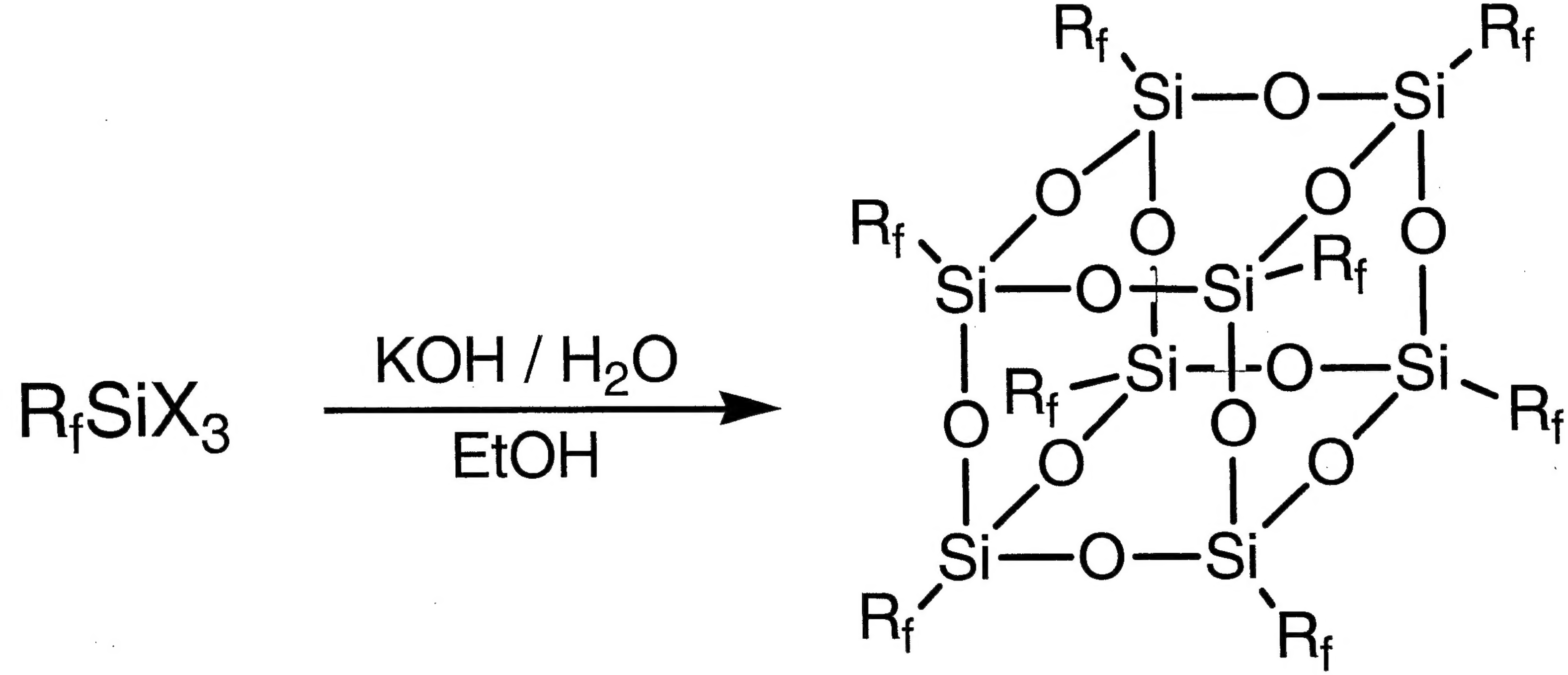




Incompletely condensed

Brown, Feher, AFRL, Hybrid Plastics

Synthesis

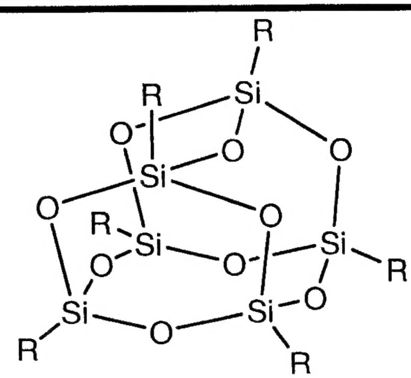


$R_{f8}T_8$

X = -OMe, -OEt

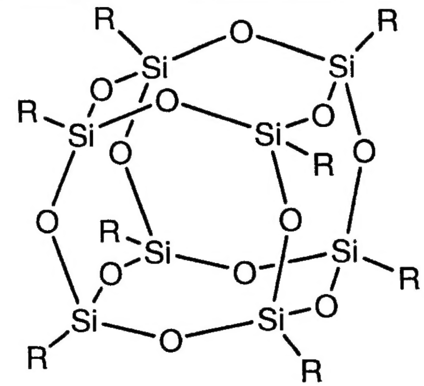
R_f = $-CH_2CH_2CF_3$, $-CH_2CH_2(CF_2)_5CF_3$, $-CH_2CH_2(CF_2)_7CF_3$

Fluorodecyl$_n$T$_n$

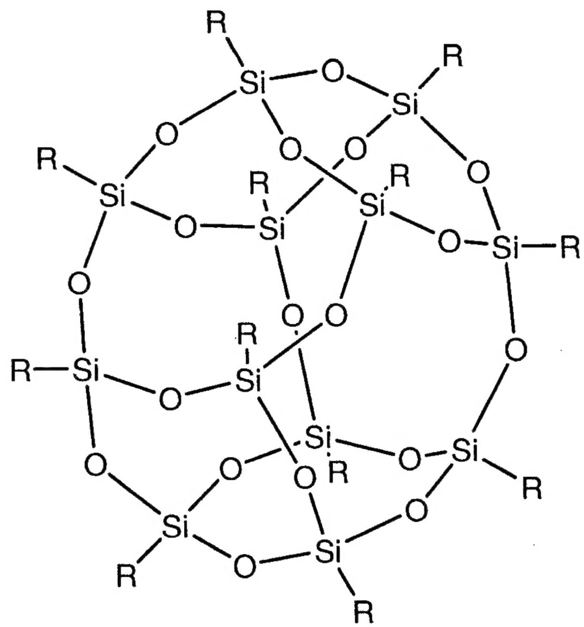


T$_6$ (~5%)

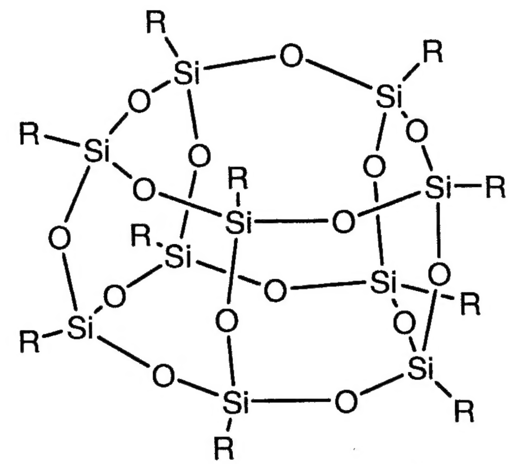
R = $-CH_2CH_2(CF_2)_7CF_3$



T$_8$ (~91%)
MW = 3993.54



T$_{12}$ (~3%)

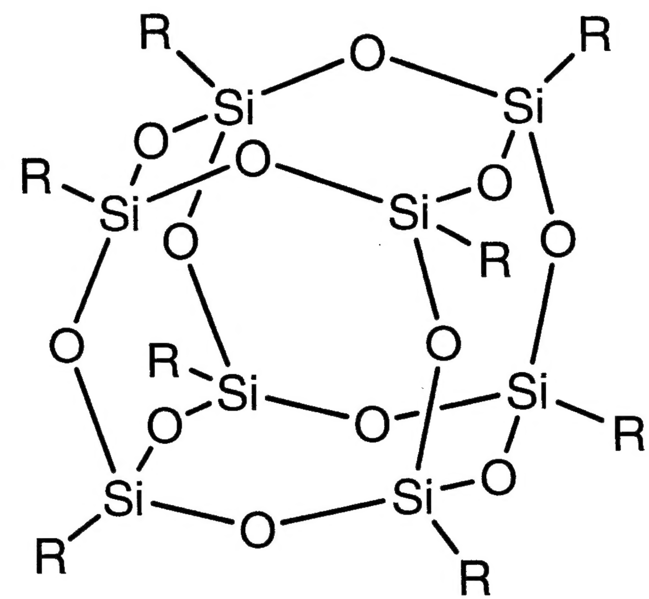


T$_{10}$ (~1%)

100% Fluorodecyl$_8$T$_8$

$R = -CH_2CH_2(CF_2)_7CF_3$

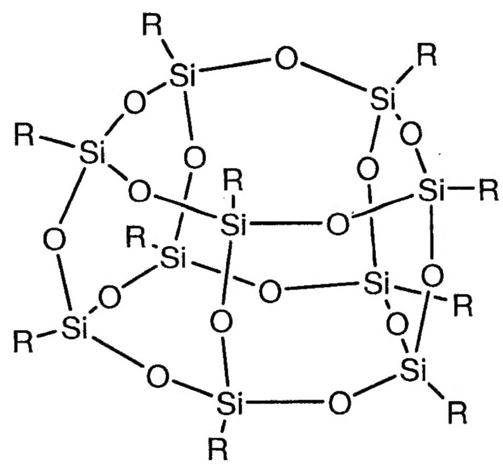
MW = 3993.54



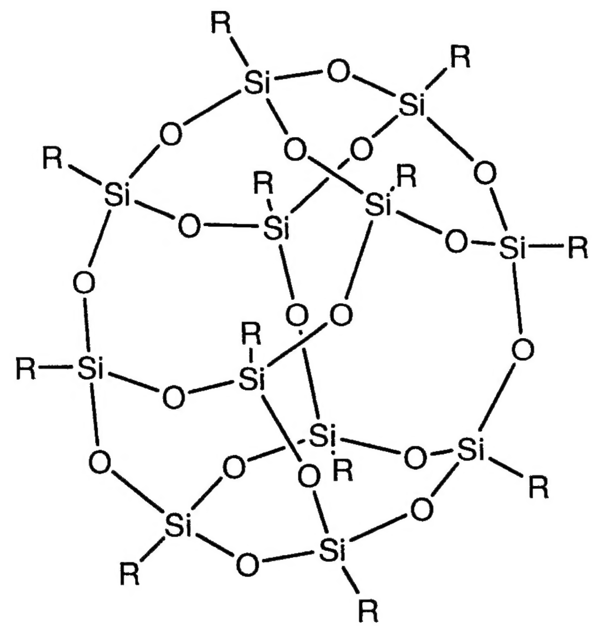
T_8

3,3,3-Trifluoropropyl$_n$T$_n$

R = $-CH_2CH_2CF_3$



T_{10} (~11%)



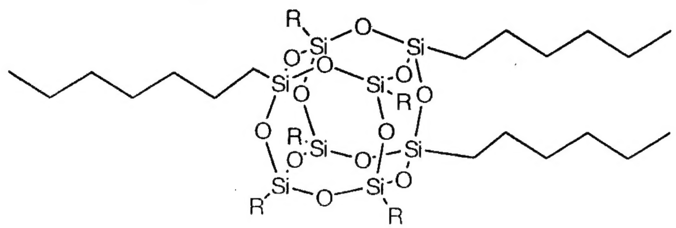
T_{12} (~89%)

Why Fluorinated POSS?

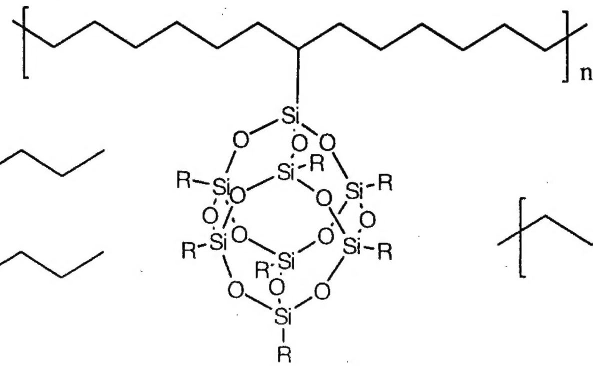
Fluorinated POSS may be useful:

- To make spacecraft coatings resistant to atomic oxygen
- In creep-resistant fluoropolymer seals and gaskets
- In hydrophobic surfaces

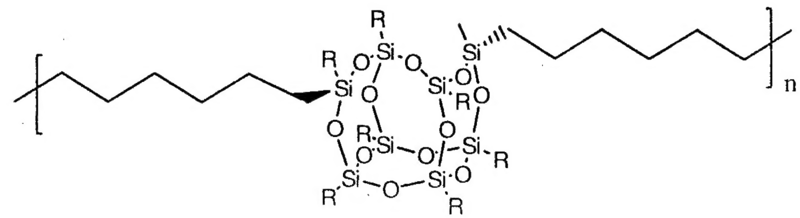
POSS Polymer Incorporation



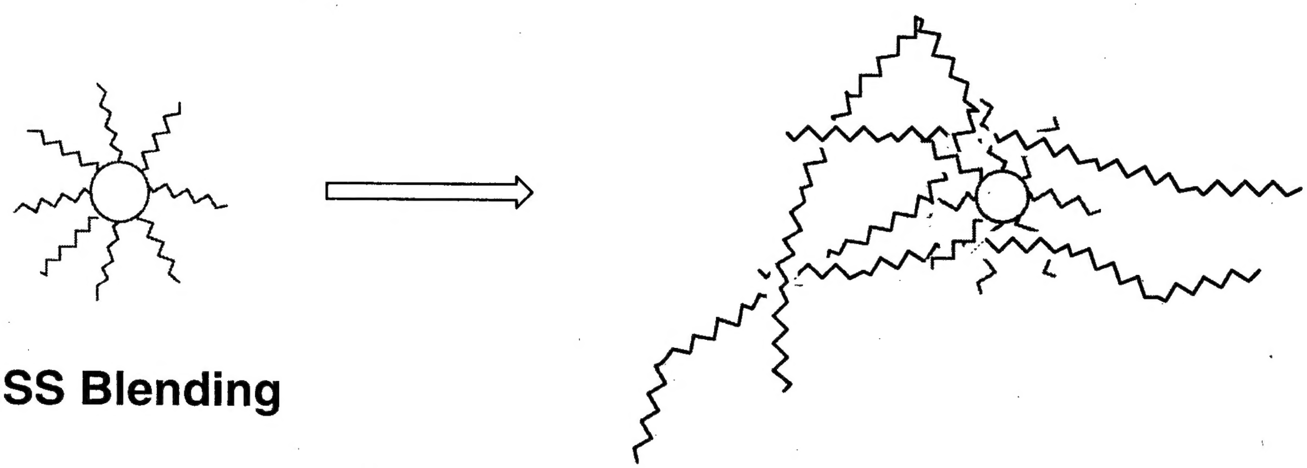
Cross-linker



POSS Pendant



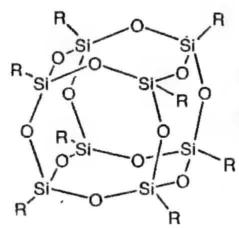
Bead Copolymer



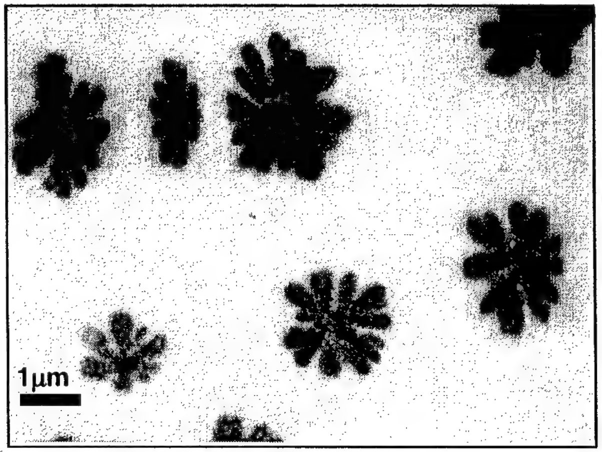
POSS Blending

Importance of R groups: Affect compatibility with polymer matrix

50 Wt % POSS Blends in 2 Million MW PS

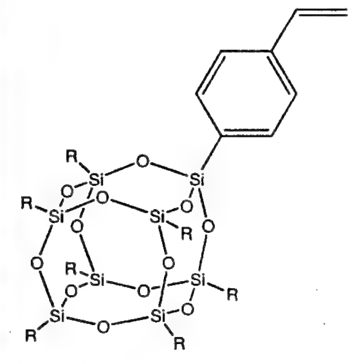


Cp_8T_8

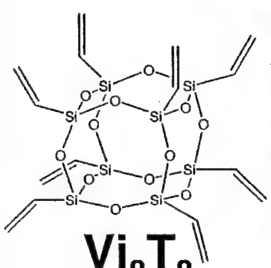


Domain Formation

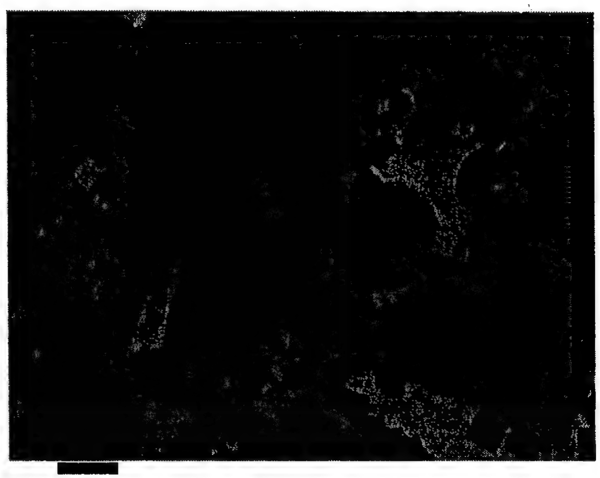
Partial Compatibility



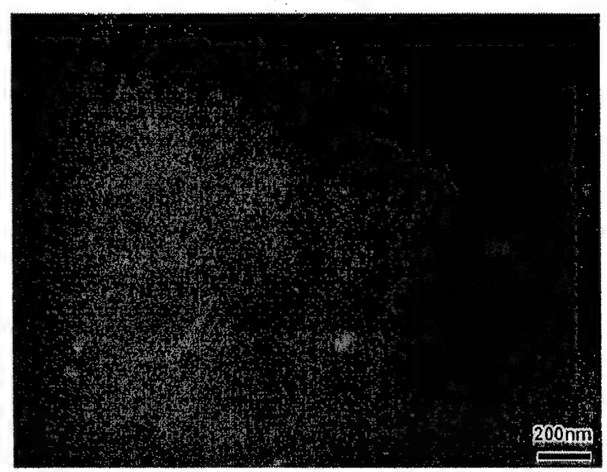
Cp_7T_8Styryl



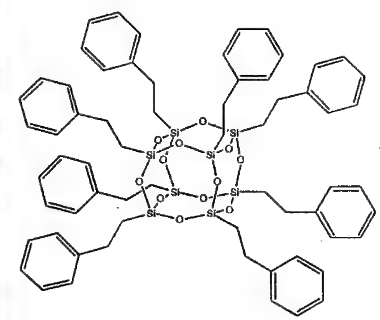
Vi_8T_8



Immiscible POSS Crystallites



Complete Compatibility-
POSS Nanodispersion/Transparent



$Phenethyl_8T_8$

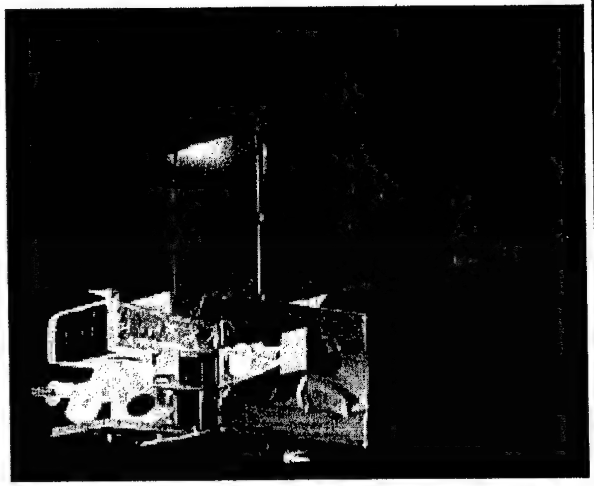
Blanski, et al., *Polymer Preprints*, **2000**. 41(1): p. 585.

Space Applications

LEO Environment
(Altitudes of 200 to 1500 km)

- Atomic Oxygen
  - Formed from photo-dissociation of O_2 in atmosphere.
  - Actual flux on spacecraft traveling at 8 to 12 km/s ~10^{15} atoms/cm^2•s
  - collision energy ~ 5eV (C-C ~ 4 eV, C-N ~ 3 eV)
- Low-energy and high energy charged particles.
- Thermal cycling -50 to 150°C
- Solar UV and VUV radiation
  - VUV wavelengths in LEO extend below 290nm.
  - Bond scission and radical formation can lead to embrittlement.

Goal: Develop Multi-Functional, Space-Survivable Materials



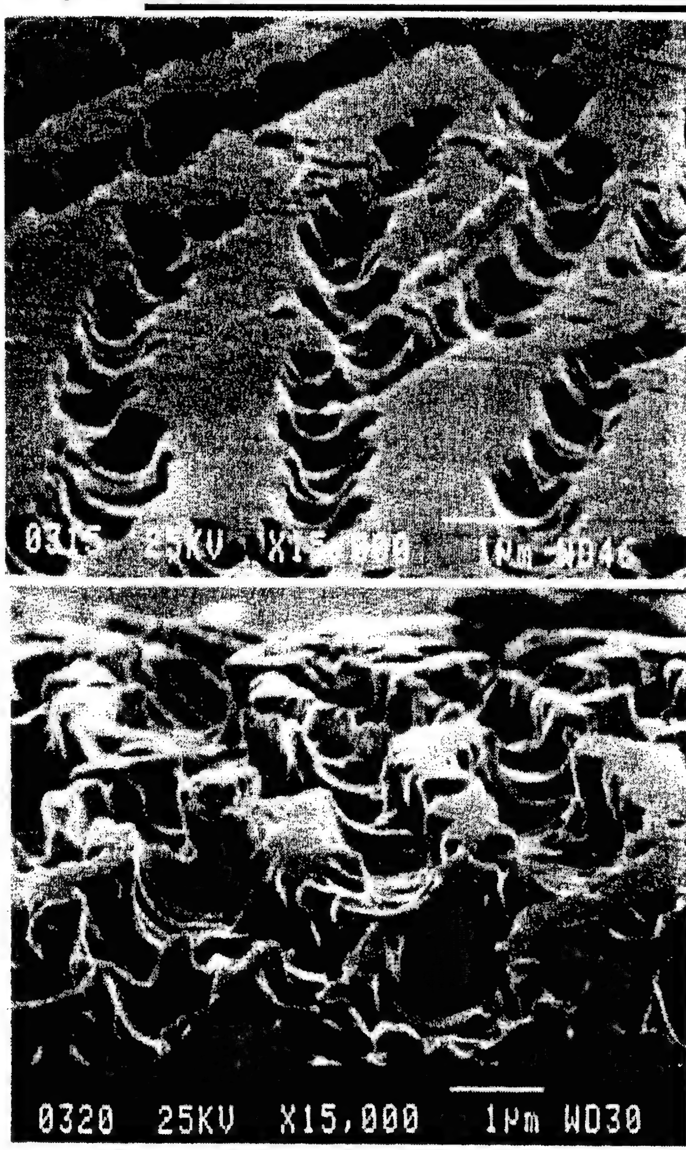
Satellites & Space Systems

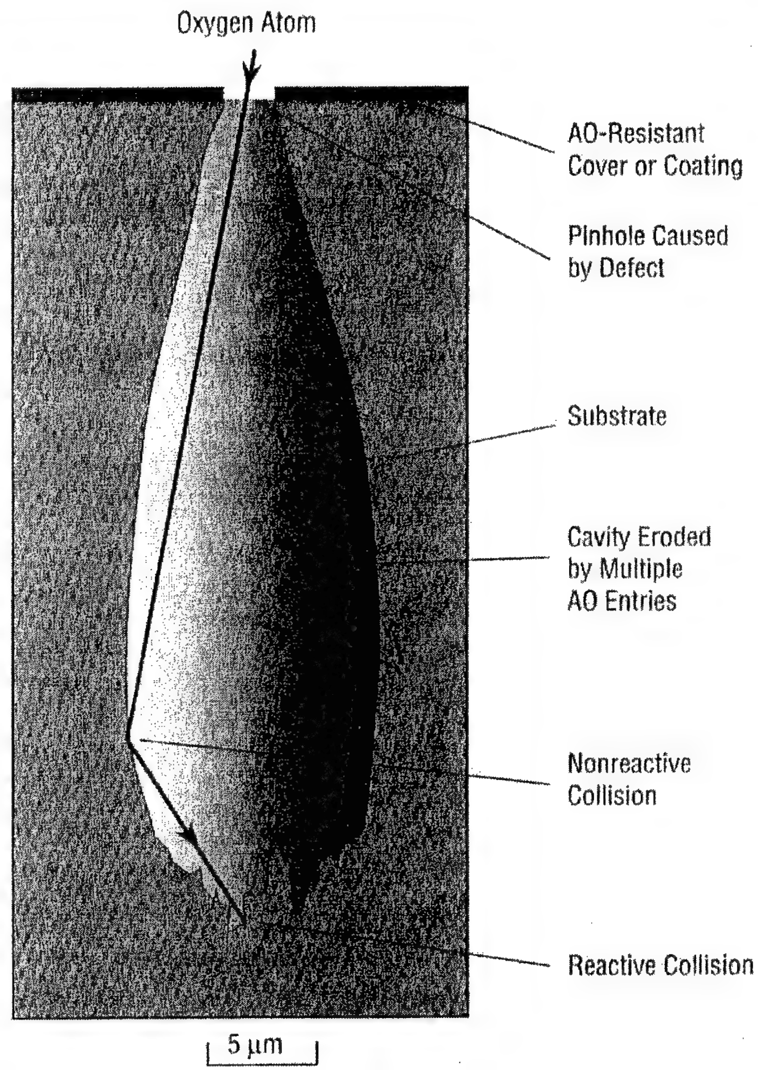
Bond	Dissociation Energy (EV)	λ (nm)	Material
$-C_6H_4-C(=O)-$	3.9	320	Kapton®
C-N	3.2	390	Kapton®
CF_3-CF_3	4.3	290	FEP Teflon®
CF_2-F	5.5	230	FEP Teflon®
Si-O	8.3	150	Nanocomposite
Zr-O	8.1	150	Nanocomposite
Al-O	5.3	230	Nanocomposite

Objectives

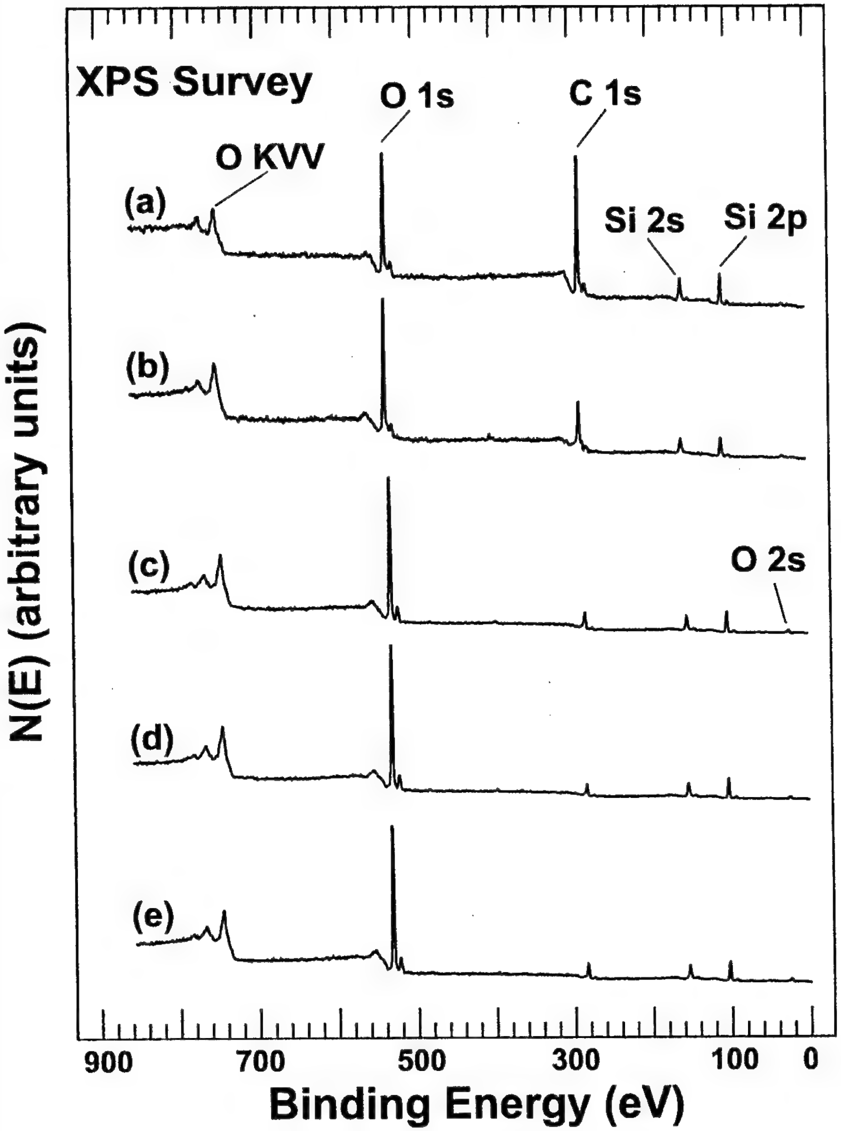
- Increase Space Resistance (AO, particle & VUV radiation, thermal cycling) of Polymeric Materials
- Self-Passivating/Self-Rigidizing/Self-Healing based on nanocomposite incorporation

AO undercutting of LDEF Aluminized-Kapton Multilayer Insulation

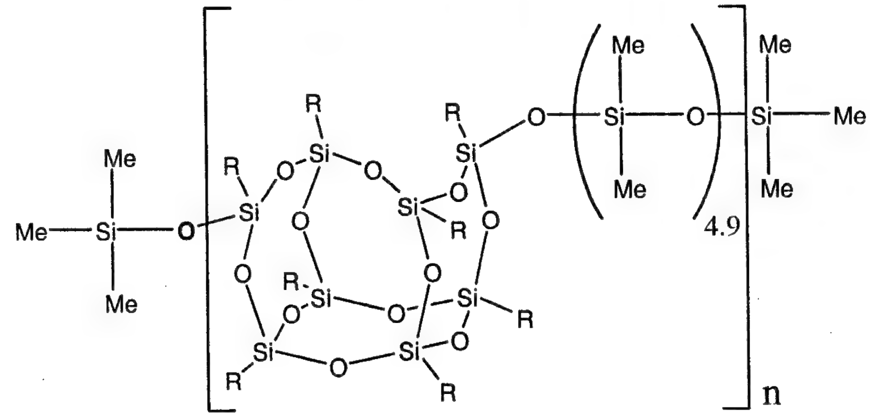




DeGroh, K.K., Banks, B.A., J. Spacecraft and Rockets, Vol. 31, No. 4, 656-664 (1994)



POSS Siloxane



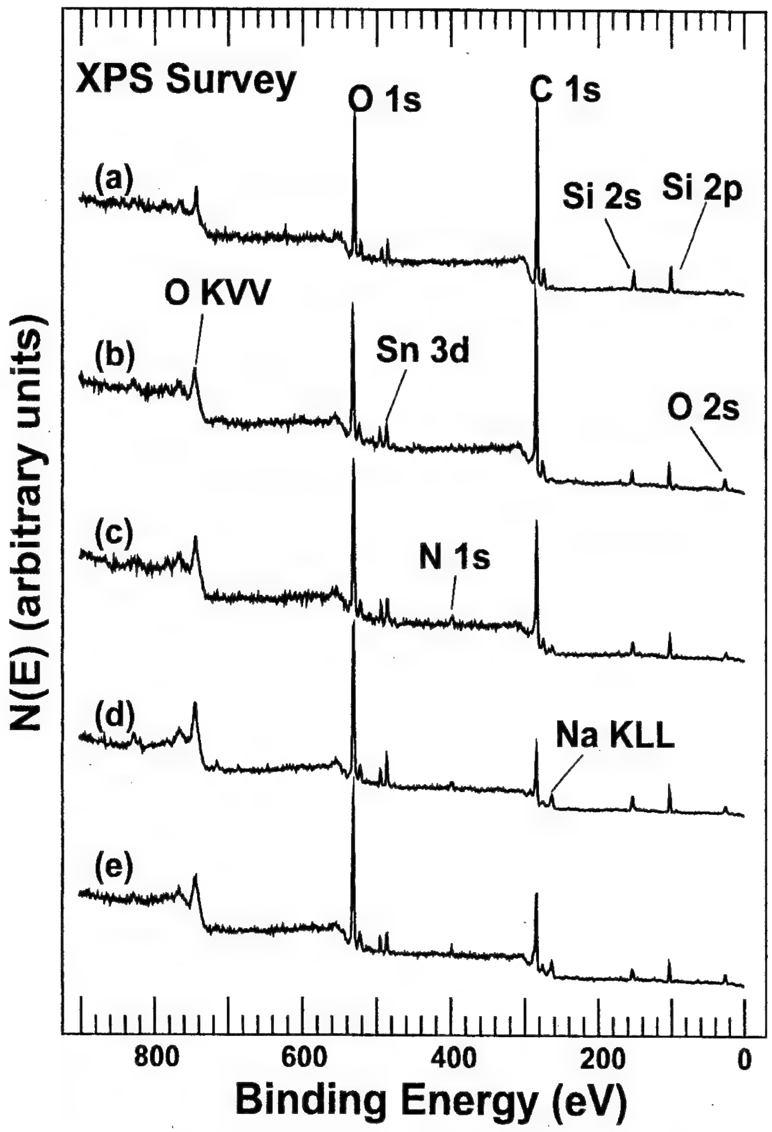
Composition, at %

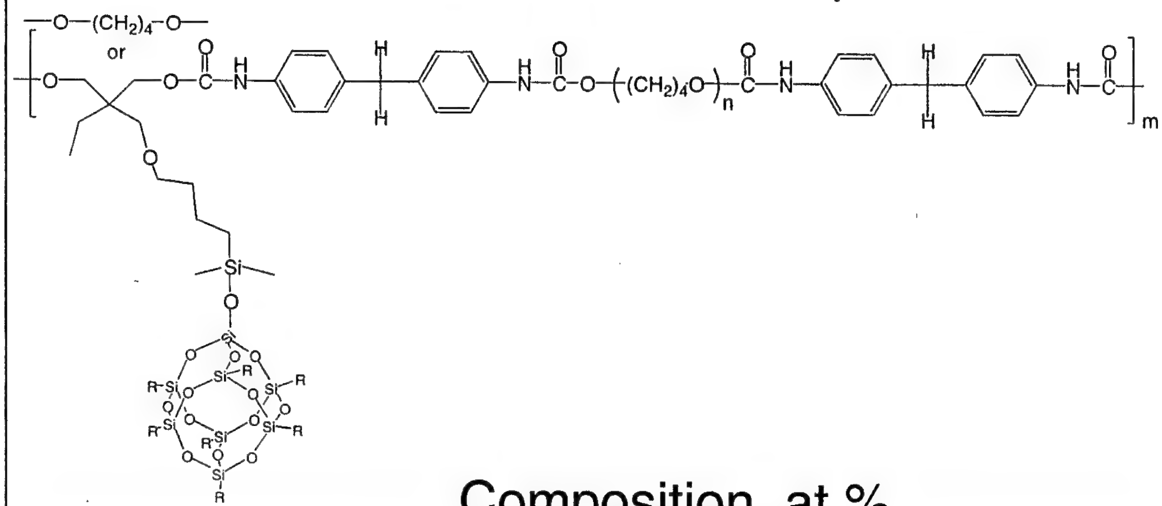
Sample Treatment	O	C	Si
As entered	18.5	65.0	16.6
2.0 hr	33.8	48.4	17.8
24.6 hr	49.1	22.1	28.8
63.0 hr	55.7	16.3	28.0
4.8 hr air	52.8	19.5	27.7

Gonzalez, R. I., Phillips, S. H., Hoflund, G. B., *J. of Spacecraft and Rockets*, Vol 37, No. 4, **2000**, pp. 463-467.

XPS survey spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.

60 wt % POSS-Polyurethane





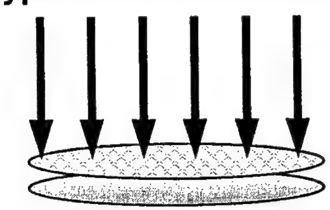
Composition, at %

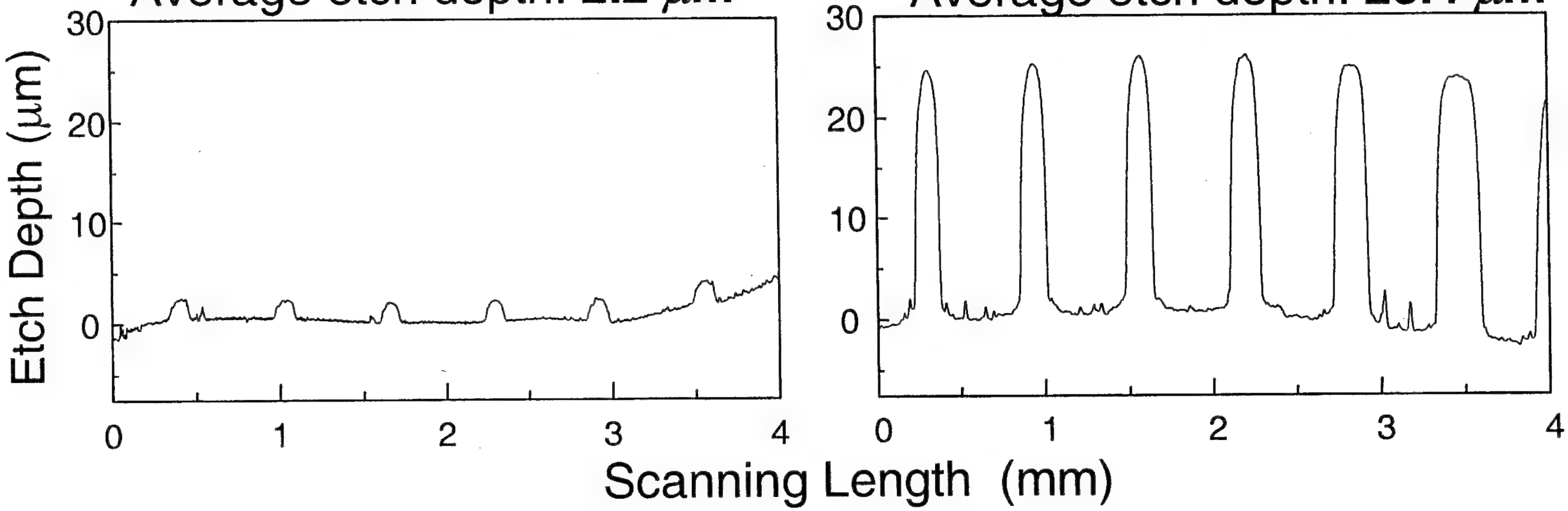
Sample Treatment	O	C	Si	Sn	Na	N
As entered	18.2	70.1	11.3	0.4	-	-
2.0-hr	17.5	70.2	11.2	0.7	0.4	-
24.0-hr	23.7	58.2	13.2	0.9	1.4	2.6
63.0-hr	35.3	37.3	20.4	1.3	3.0	2.7
3.3-h air	31.6	48.5	14.6	1.0	2.7	1.6

Phillips, S. H., Hoflund, G. B., Gonzalez, R. I., 45th International SAMPE Symposium, 2000, Vol. 45, No. 2, pp. 1921-1931.

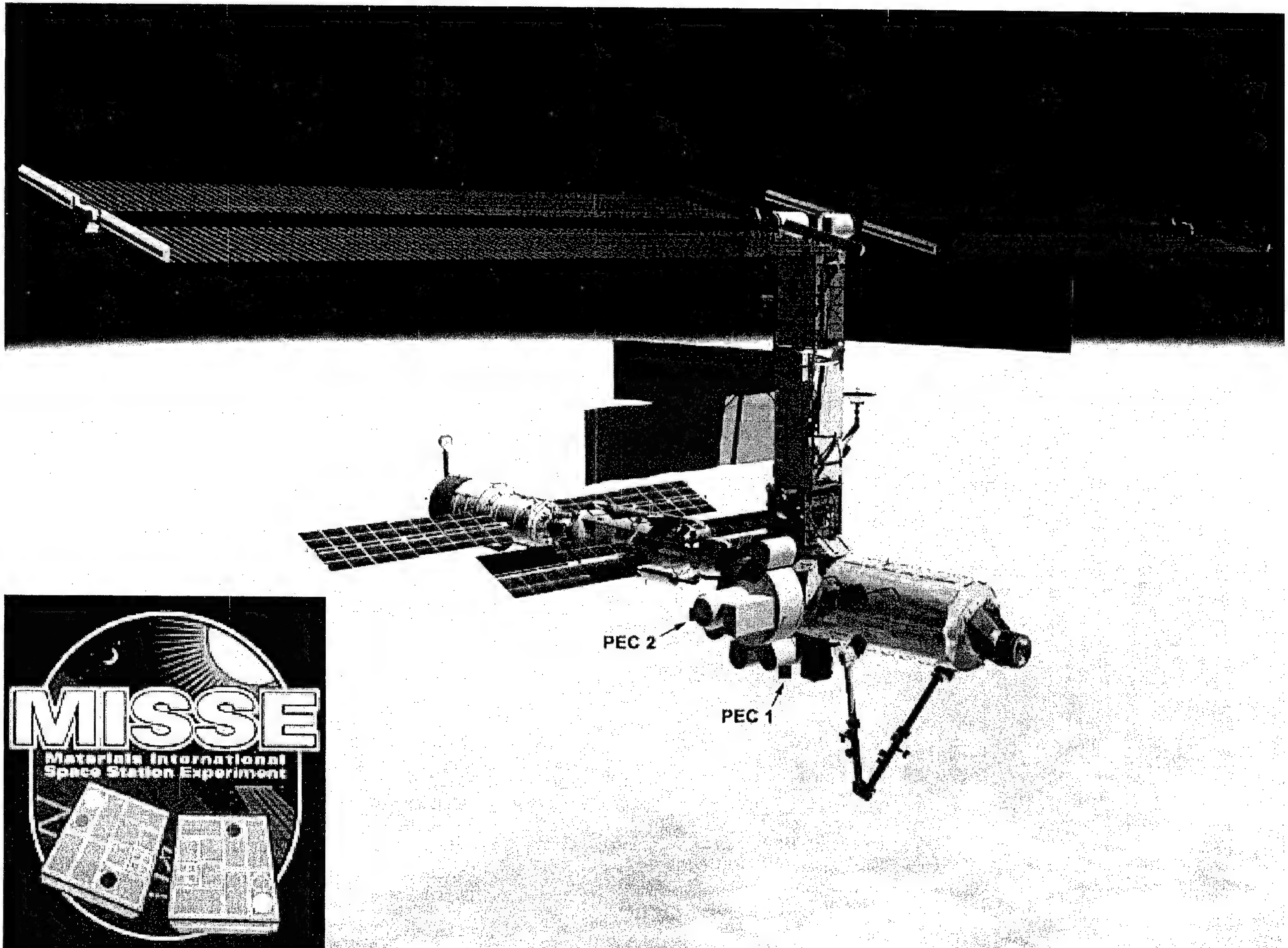
XPS Survey Spectra from a 60 wt % POSS-PU (a) after insertion into the vacuum system, (b) after a 2-hr (c) 24-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 3.3-hr air exposure following the 63-hr exposure.

O-Atom Etching Experiment (~10 DAYS IN LEO)
Total AO fluence of 8.47×10^{20} atoms cm^{-2} (100,000 pluses)





Significantly improved oxidation resistance due to a rapidly formed ceramic-like, passivating and **self-healing** silica layer preventing further degradation of underlying virgin polymer.


PEC 2
PEC 1
MISSE
Materials International
Space Station Experiment

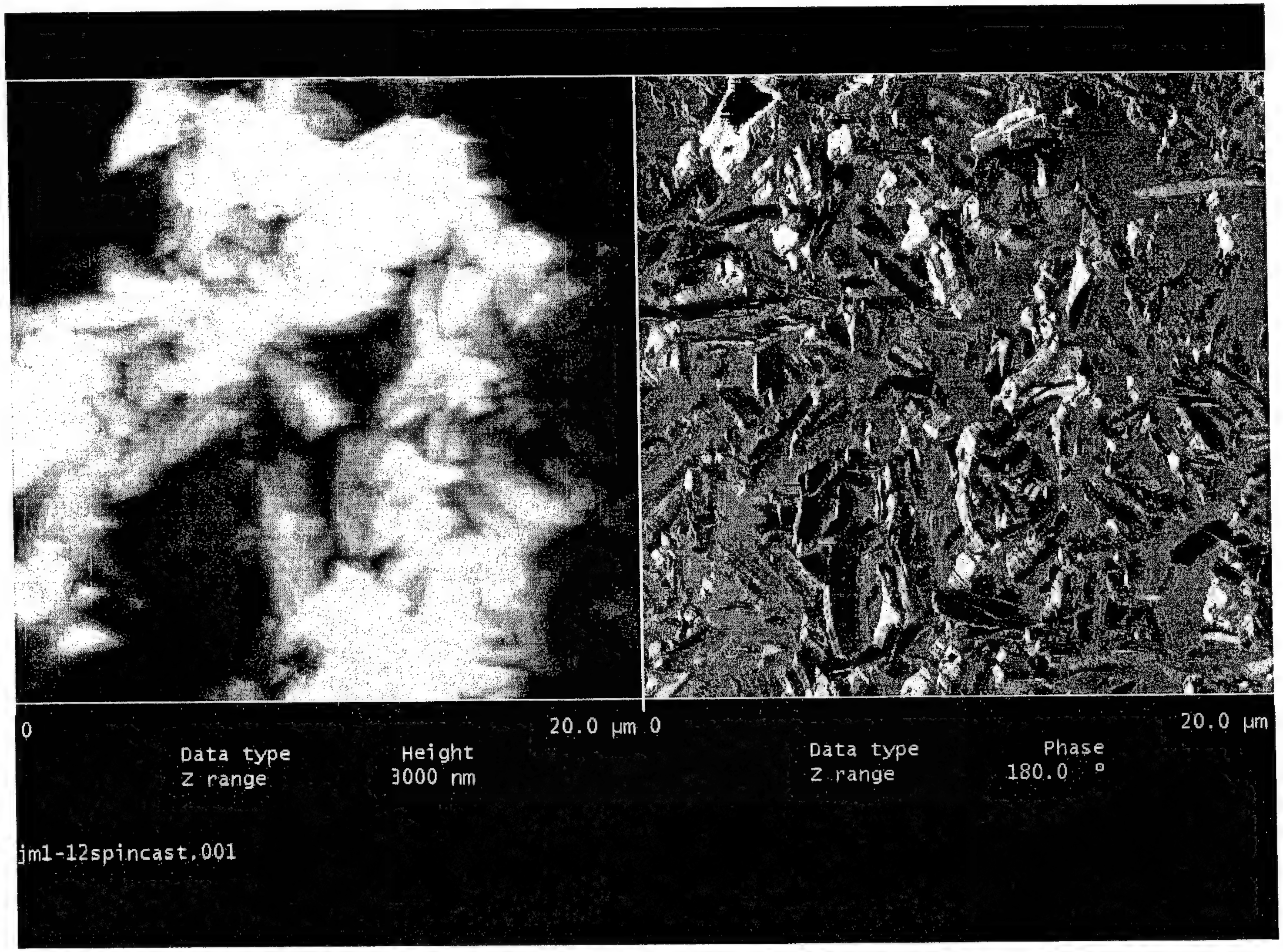
Creep Resistant Seals and Gaskets

- Fluoropolymers are resistant to organic fuels and fluids.
- Creep is the change in dimensions of a molded part resulting from cold flow incurred by continual loading.
- Creep can cause a press-fit to loosen or even fail.
- PTFE has a low tensile strength (2500–3000 psi at break).
- Tensile strength is a very important factor.
- POSS may reduce the amount of creep as well as enhance thermal and mechanical properties.
- POSS can be blended with most fluoropolymers.
- Supercritical methods may allow fluorinated POSS to be incorporated into PTFE.

Surface Properties

- Fluorinated polymers are used for non-stick coatings and hydrophobic surfaces.
- Blended POSS may further decrease the surface energy of fluorinated polymers.
- One way to measure surface energy is to measure the contact angle of a drop of water on the surface.
- These low surface energy polymers may lead to anti-icing or non-wetting applications.

AFM Image of Spin-Cast Fluorodecyl$_n$T$_n$ Surface

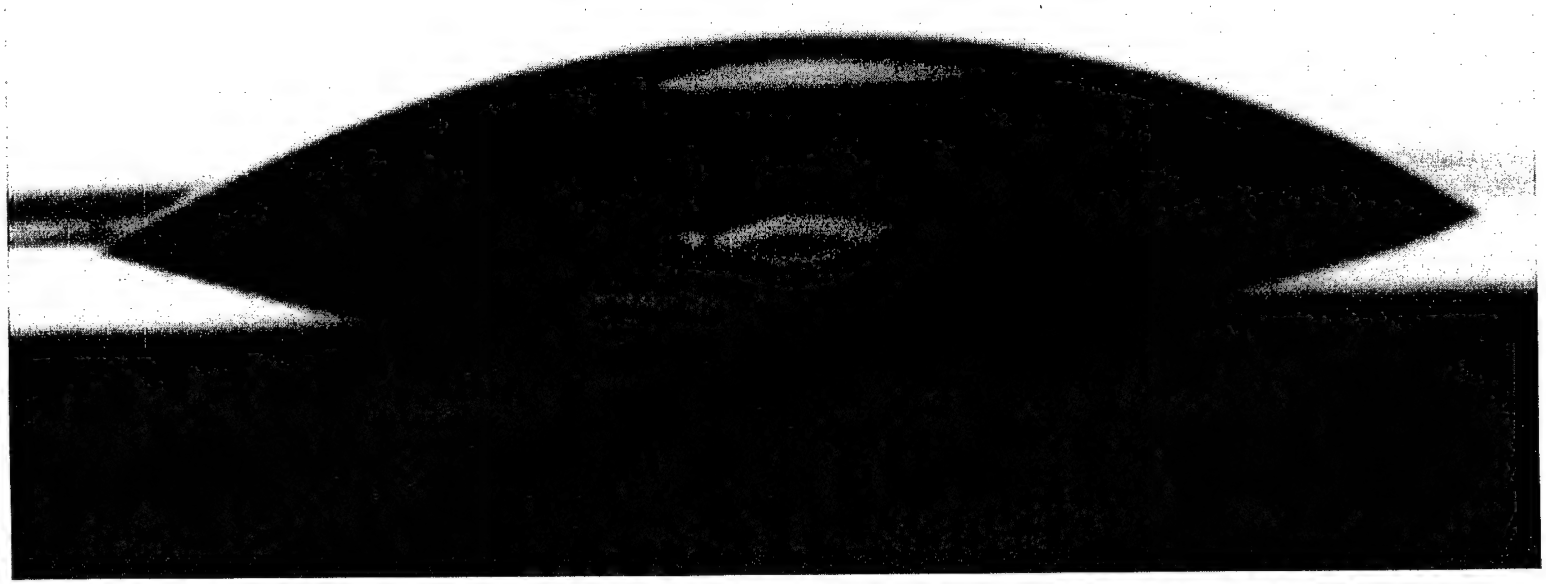


Conatct Angle of Water on Mica ~32°

12/12/02

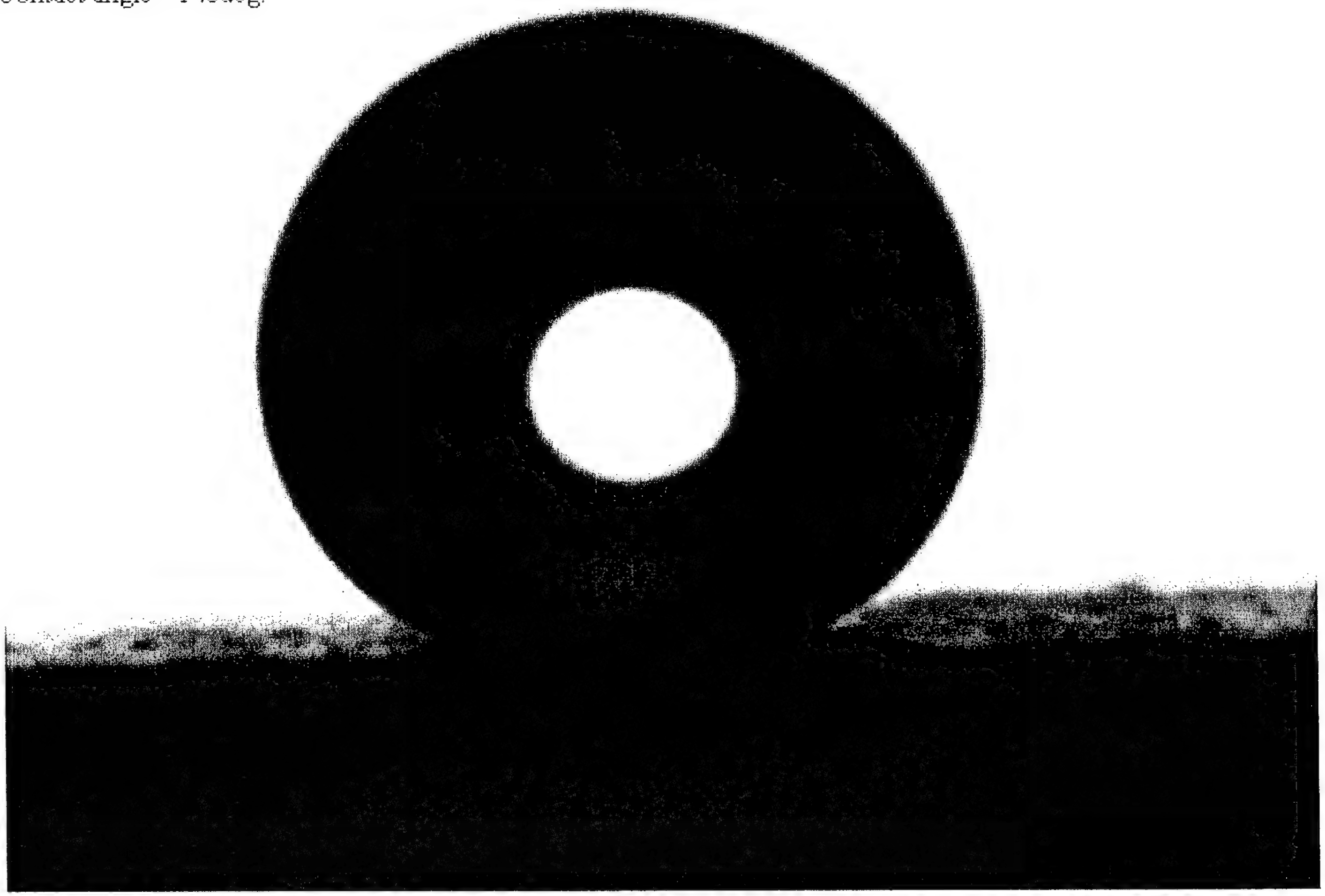
a drop of water on a freshly cleaved mica surface in air and at room temperature.

Contact angle ~ 32 deg.



Conatct Angle of Water on Fluorodecyl POSS film ~140°

12/12/02
a drop of water on a flourinated mica surface in air and at room temperature.
Contact angle ~ 140deg.

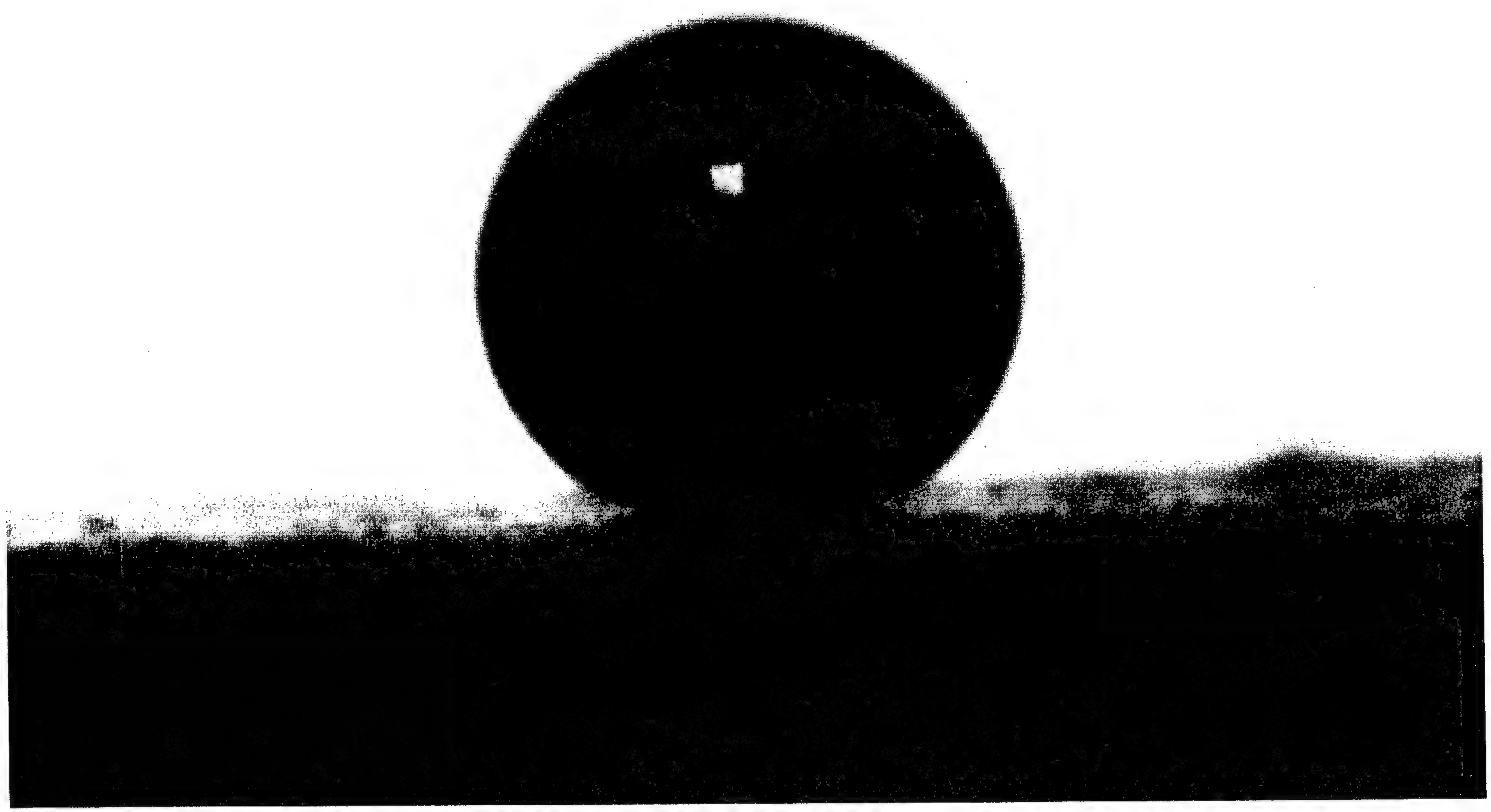


30° Higher than PTFE

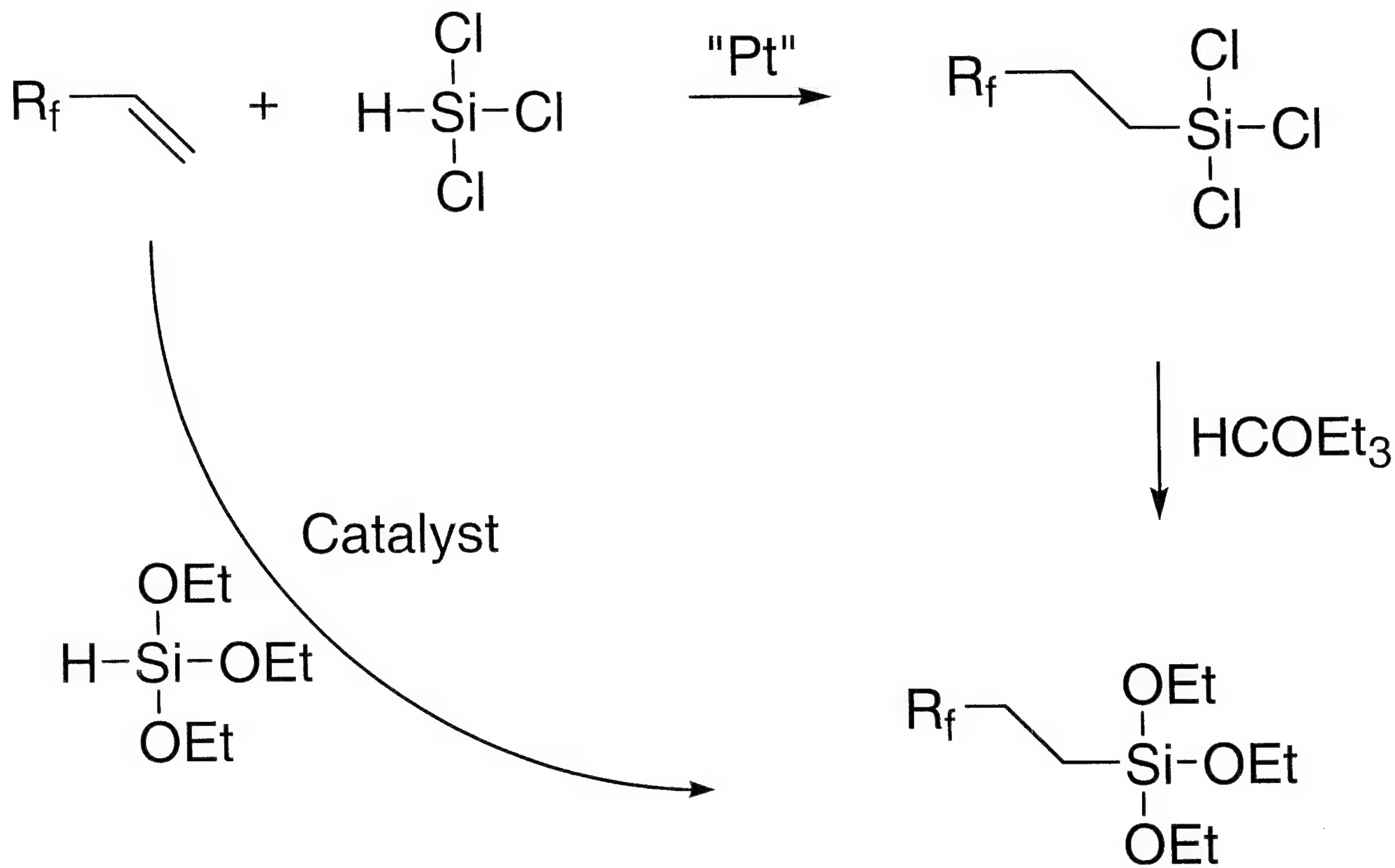
Conatct Angle of Mercury on Fluorodecyl POSS film ~145°

12/12/02
A drop of mercury on fluorinated mica surface in air and at room temperature.

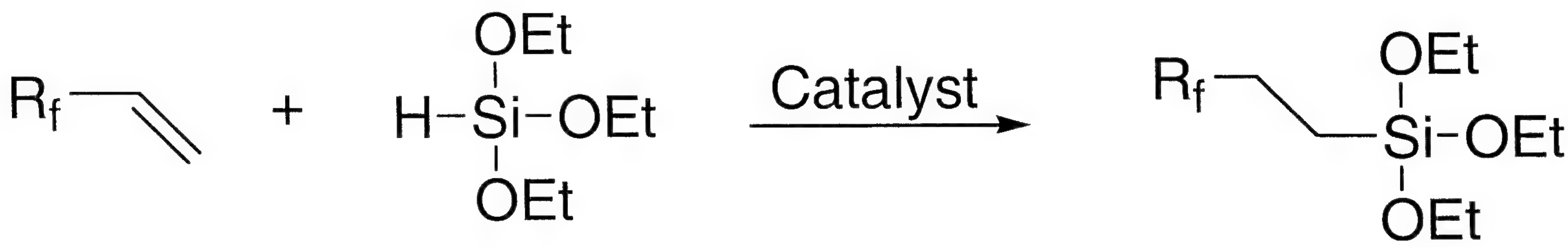
Contact angle~ 145deg.



Hydrosilylation



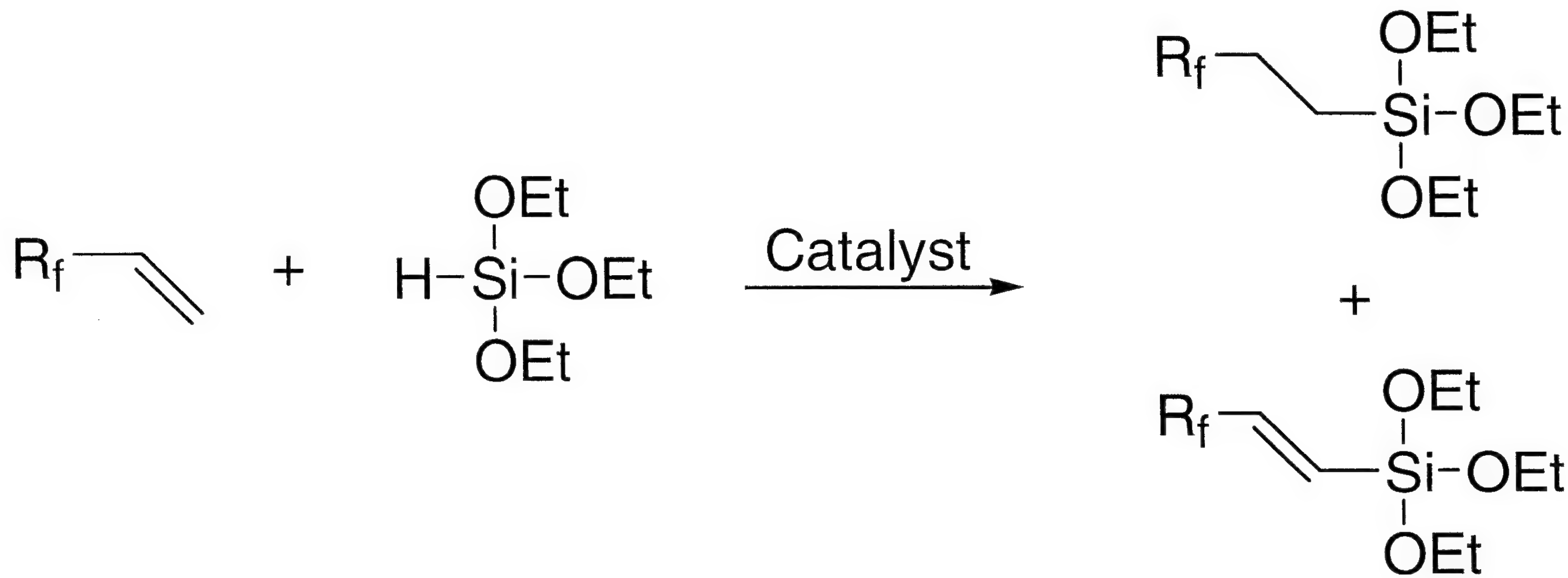
Hydrosilylation



Catalyst	Result
Karstedt (Pt)	No Reaction
H_2PtCl_6 (Pt)	No Reaction
$RuH_2(CO)(PPh_3)_3$	< 50% Yield
$RhCl(PPh_3)_3$	~ 50% Yield
$Co_2(CO)_8$	Underway

Yield based on methylene to vinyl proton ratio in ^1H NMR.

Side Reaction



Problem:
Dehydrogenative silylation product also gives vinyl peaks in ^{1}H NMR spectra

Summary

Fluorinated POSS may be useful to make spacecraft coatings resistant to atomic oxygen by forming a silica-like passivating layer.

Fluorinated POSS may be useful in fluoropolymer seals and gaskets to increase mechanical strength and improve creep characteristics.

Fluorinated POSS may also be useful to decrease surface energy in hydrophobic surfaces.

Acknowledgements

The Polymer Working Group at Edwards Air Force Base is:

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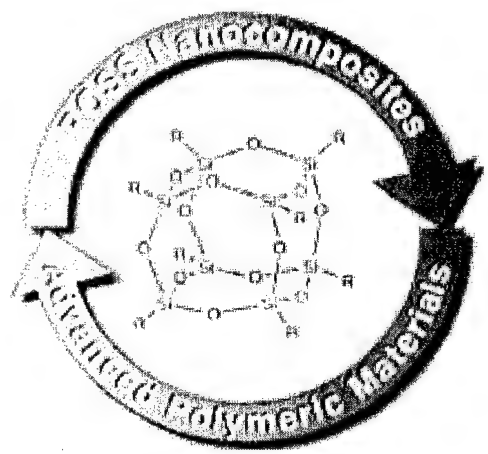
Mr. Brian Moore
Dr. Brent Viers
Dr. Darrell Marchant



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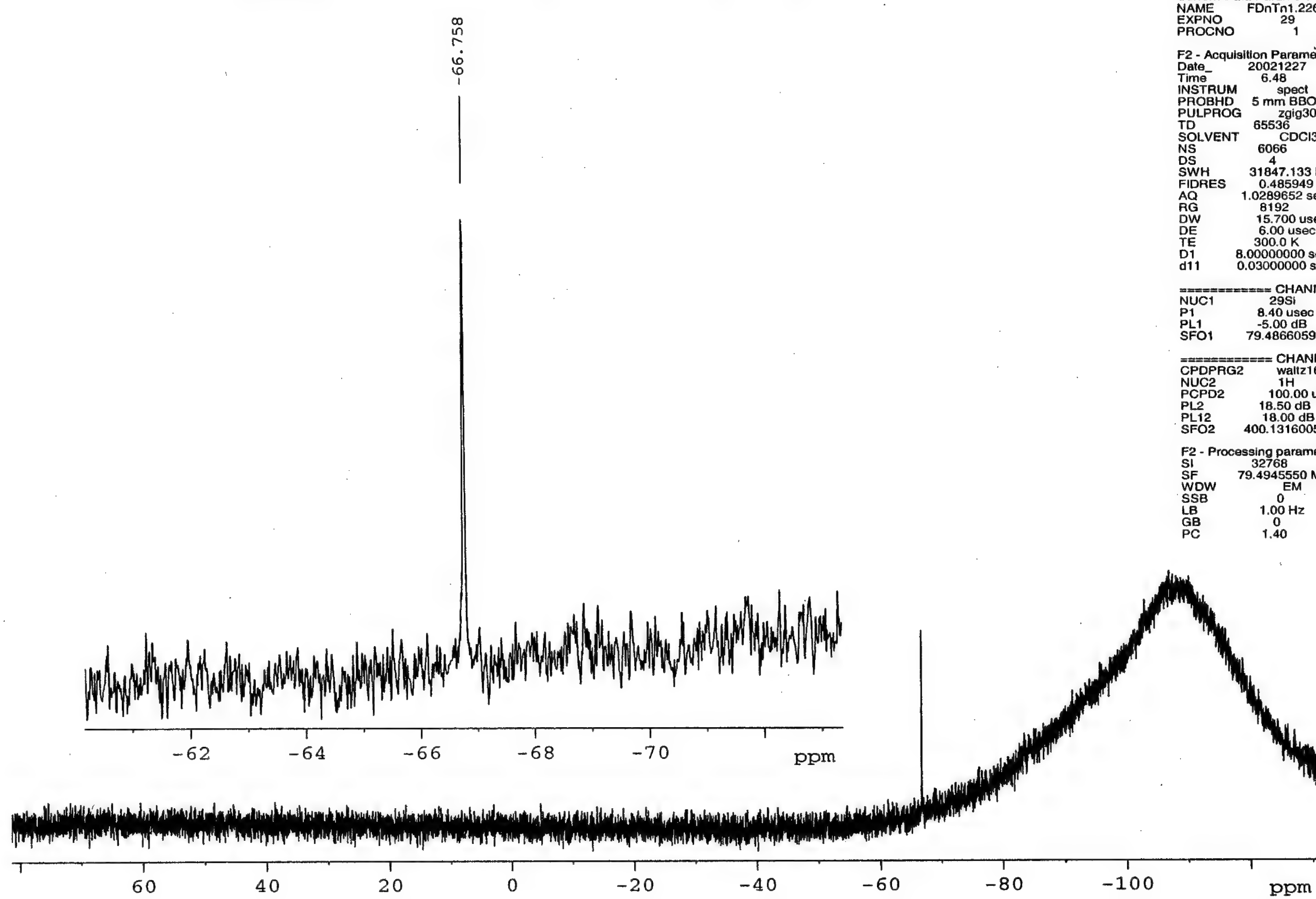
Mrs. Becky Morello
Dr. Rusty Blanski
Dr. Joe Mabry
Mrs. Sherly Largo
Dr. Tim Haddad

Financial $upport:
Air Force Office of Scientific Research
Air Force Research Laboratory, Propulsion Directorate

Backup Slides

100% Fluorodecyl$_8$T$_8$

4jm1-32 Fluorodecyl8T8 after extraction Mabry 12-27-02



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DE	6.00 usec
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d11	0.03000000 sec

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PL1	-5.00 dB
SFO1	79.4866059 MHz

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PL12	18.00 dB
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F2 - Processing parameters

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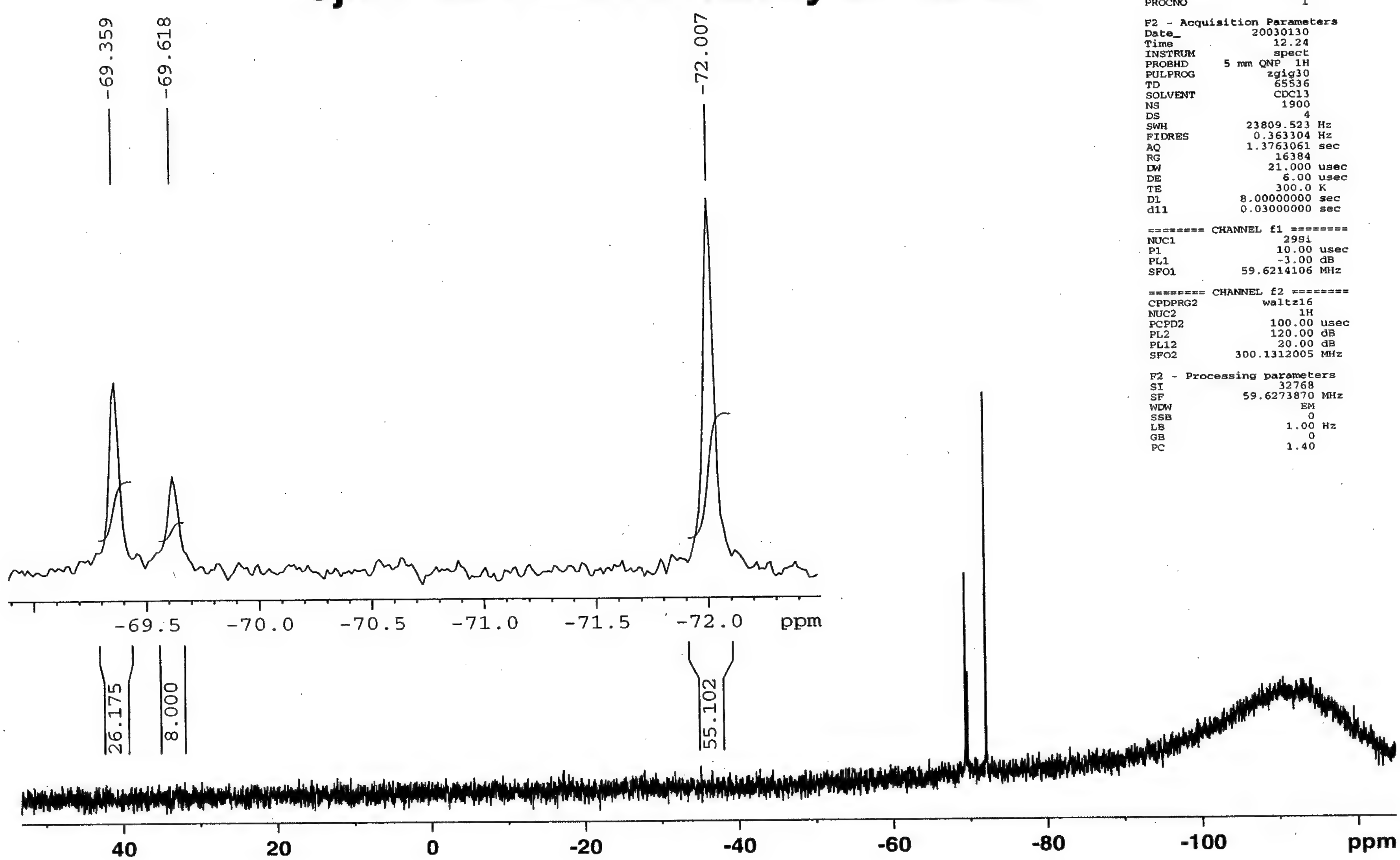
3,3,3-Trifluoropropyl$_n$T$_n$

3jm1-43 TFPnTn Mabry 01-30-03

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PROCNO                   1

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NS                    1900
DS                       4
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FIDRES            0.363304 Hz
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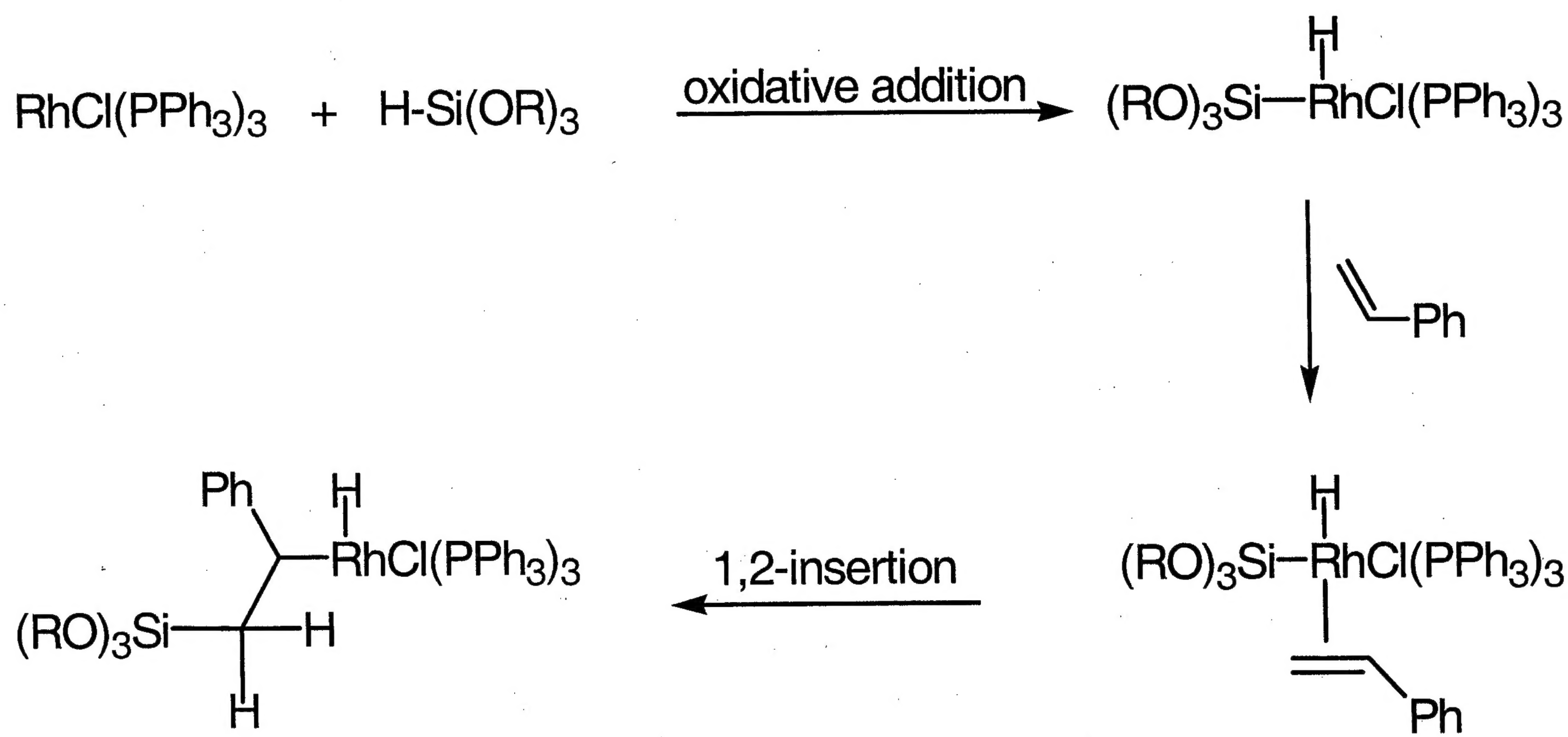
RG                   16384
DW                  21.000 usec
DE                    6.00 usec
TE                   300.0 K
D1              8.00000000 sec
d11             0.03000000 sec

======== CHANNEL f1 ========
NUC1                  29Si
P1                   10.00 usec
PL1                  -3.00 dB
SFO1           59.6214106 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                 120.00 dB
PL12                 20.00 dB
SFO2          300.1312005 MHz

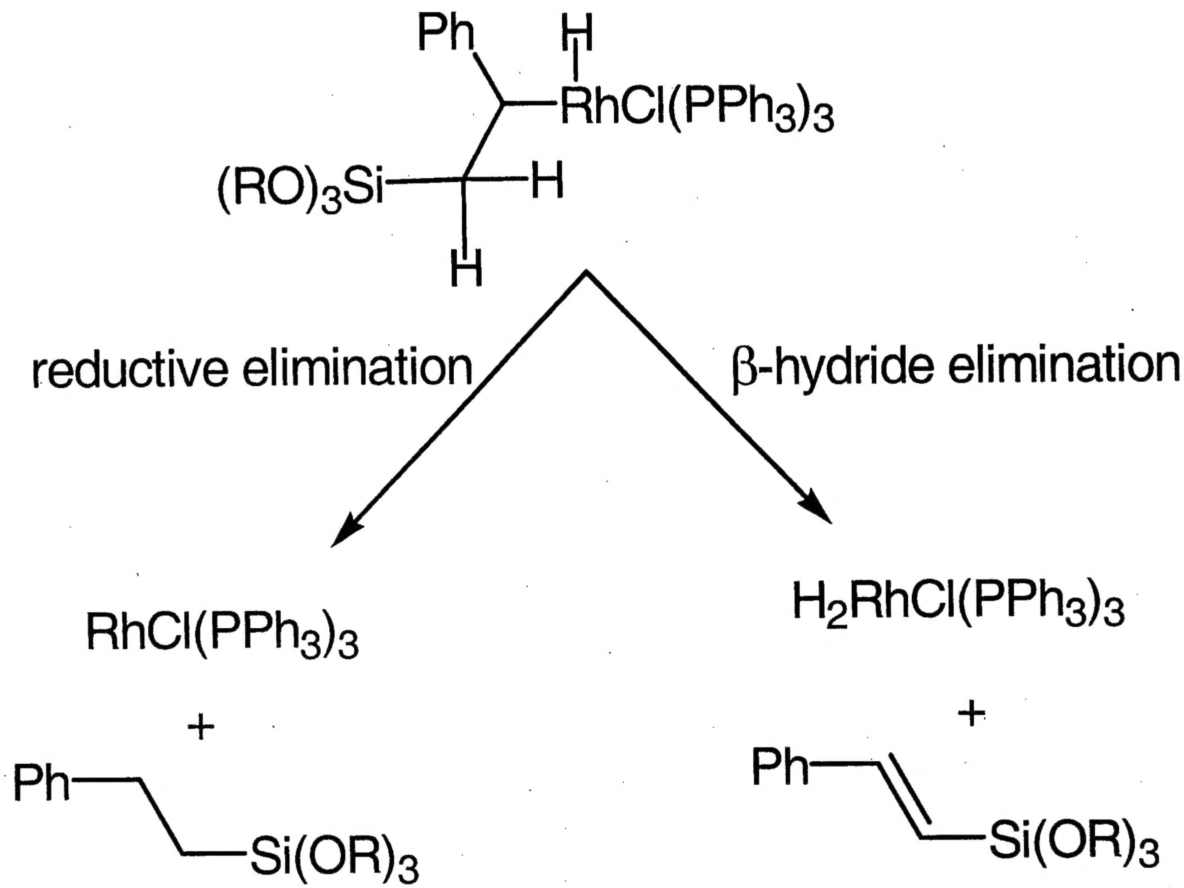
F2 - Processing parameters
SI                   32768
SF              59.6273870 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

Mechanism



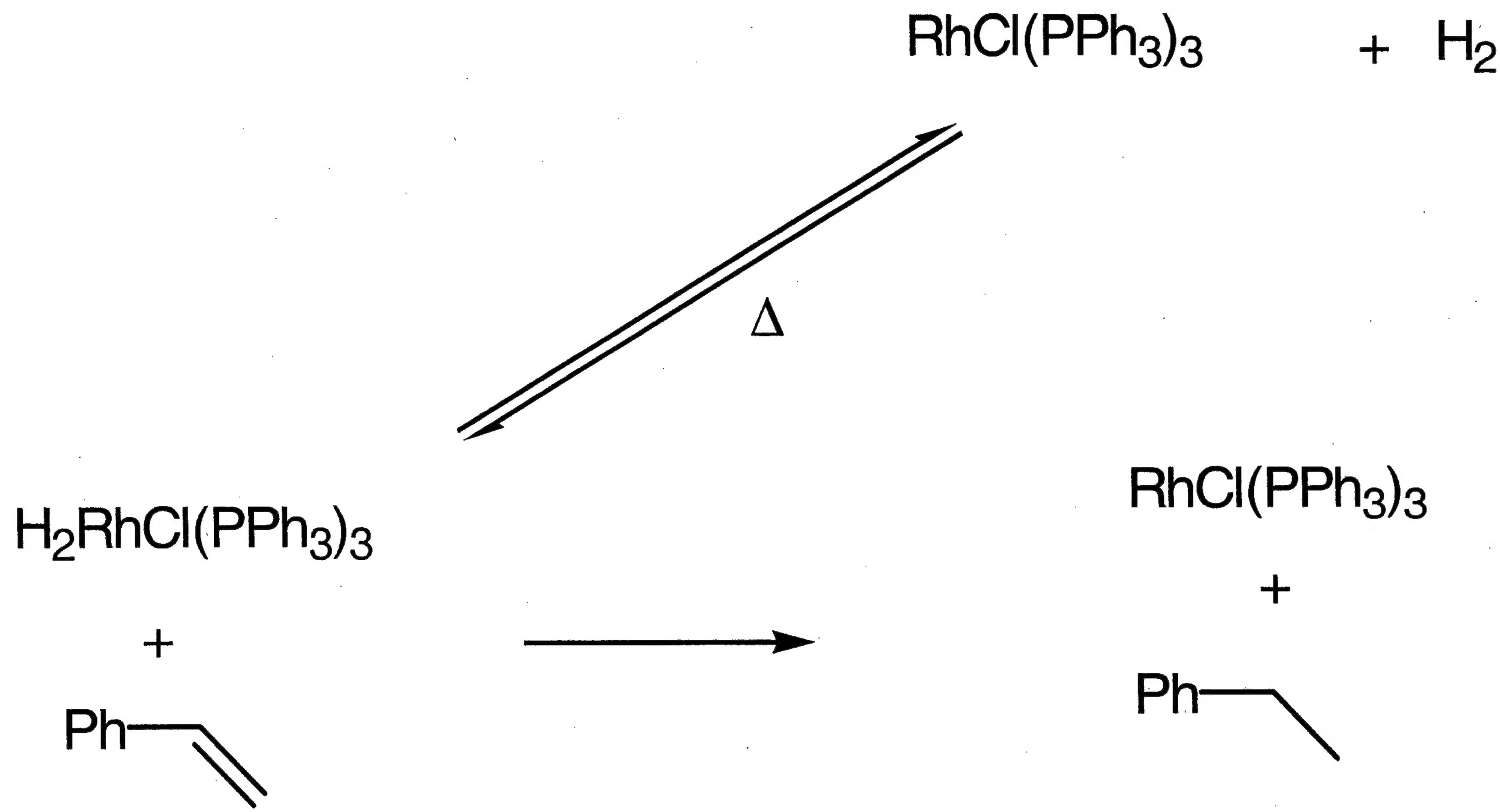
RhCl(PPh3)3 + H-Si(OR)3
oxidative addition
(RO)3Si—RhCl(PPh3)3
H
Ph
1,2-insertion

Mechanism



Hydrosilylation competes with dehydrogenative silylation.

Mechanism



Rh species produced by β-hydride elimination hydrogenates unreacted alkene.

Surface Energy of Fluorosiloxanes

Polymer	Surface Energy (mJ/m^2)
Poly(methylheptadecafluorodecylsiloxane)	7.0
Poly(methylnonafluorohexylsiloxane)	9.5
Poly(methyltrifluoropropylsiloxane)	13.6
Poly(dimethylsiloxane) (PDMS)	22.8
Poly(tetrafluoroethylene) (PTFE)	19.1